Macrocyclic aromatic polysulfones and sulfide-sulfones: synthesis and structural characterisation of molecular pentagons and rectangles†

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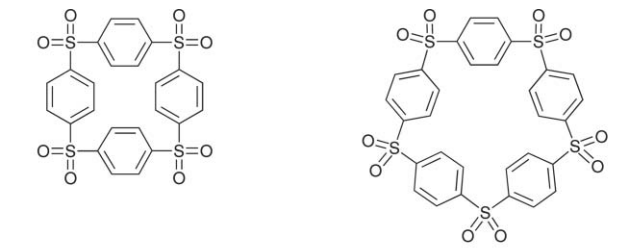
Cyclo-condensation of arylenedithiols with bis(4-chlorophenylenesulfone)s under *pseudo*-high-dilution conditions affords macrocyclic aromatic sulfide-sulfones which are readily oxidised to all-sulfone-linked macrocycles. The cyclic pentamer of poly(1,4-phenylenesulfone) and cyclic dimer of poly(1,4-phenylenesulfonyl-4,4′-biphenylenesulfone) have been isolated and characterised.

Introduction

Macrocyclic compounds are of considerable interest for the construction of molecular-recognition and ion-binding systems.[1] Well known examples include crown ethers,[2] cyclodextrins,[3] resorcinarenes,[4] cucurbiturils,[5] macrocyclic bipyridinium ions,[6] aromatic diimides,[7] and diimide-sulfones.[8]

Crystallographic studies have shown that the diaryl sulfone moiety tends to adopt a preferred conformation in which the planes of the aryl rings lie approximately orthogonal to the C-S-C plane: the so-called "open book" conformation.[9] It has been suggested that this conformation may be stabilised by the overlap of filled aromatic-carbon π-orbitals with a vacant *d-p* hybrid orbital on sulfur[10] [though intramolecular dipolar interactions between the aromatic *ortho*-hydrogens (δ^+) and the sulfone oxygens (δ^-) would also tend to stabilise the same conformation]. Thus, it might be expected that macrocyclic aromatic sulfones based on 1,4-linkages would adopt "box-like" conformations in which the planes of the aromatic rings lie perpendicular to the plane of the sulfur atoms. The strongly electron-withdrawing and rather rigid nature of the diaryl-sulfone unit suggest that such macrocycles have the potential to behave as π-electron-deficient molecular receptors. Unlike analogous systems based on the cationic 4,4′-bipyridinium unit,[11] they would have no requirement for counterions and would, in addition, afford a high degree of pre-organisation in any non-covalent complexation process. We have previously reported the synthesis and structure of a small, highly strained macrocyclic tetrasulfone (**1**, Fig. 1),[12] but the extreme insolubility of this rigid macrocycle has so far made complexation studies impracticable.



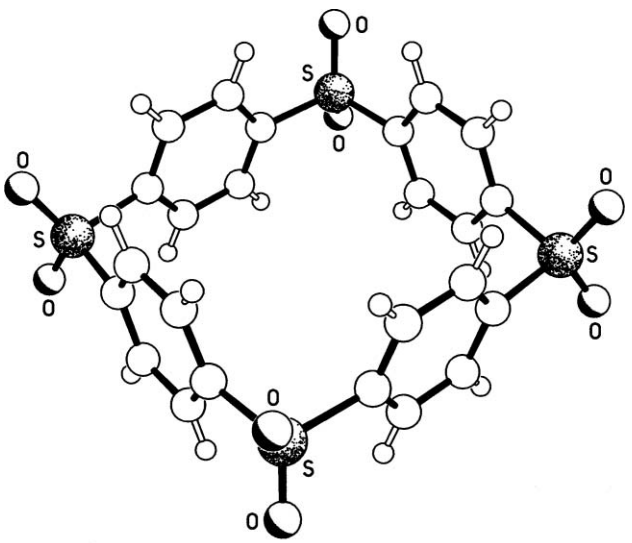


Fig. 1 X-Ray structure of the macrocyclic tetrasulfone **1** (from ref. 12).

In the present paper we report the syntheses of two somewhat larger box-type sulfone macrocycles, *via* nucleophilic

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† Electronic supplementary information (ESI) available: Details of crystallographic data collection, structure solution and refinement, including the resolution of disorder in the structure of macrocycle **6**. CCDC reference numbers 737298–737302. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912193e

cyclo-condensation of arylene dithiols with bis(4-chloroarylene-sulfone)s and peroxide-oxidation of the intermediate macrocyclic sulfide-sulfones. One final product is the pentagonal pentasulfone **2** and the other is the rectangular tetrasulfone **3**—geometrically an analogue of Stoddart's bipyridinium-based "blue box" **4**. These results confirm that the diarylene-sulfone moiety can be a useful motif for the construction of box-like molecular structures, though their relative insolubility still remains an issue for binding studies.‡

Experimental

Starting materials (*ex* Aldrich) were standard reagent grade and were used without further purification. Benzene-1,4-dithiol,[13] 9,9-dimethylfluorene,[14] 4,4′-bis(4-chlorobenzene-sulfonyl)biphenyl,[15] and 4,4′-biphenyldithiol[16] were prepared according to the literature. Thin layer chromatography was carried out on Polygram® SIL-G/UV_{254} plates. Compounds were visualised under UV light. Column chromatography was conducted on Aldrich silica gel, 230-400 mesh, 60Å. Proton NMR spectra were recorded on a Varian Unity Inova-300 spectrometer. Conventional mass spectra (EI/CI/FAB) were run on a Kratos Concept spectrometer, and MALDI-TOF MS analyses were obtained on Kratos Kompact and Micromass Tofspec instruments. Elemental analyses were provided by the analytical service of Manchester University. Melting points were determined by DSC under nitrogen using a Mettler-DSC20 system. Single crystal X-ray data for macrocycles **2**, **3**, **6** and **7** were obtained at Imperial College on a Siemens P4/RA diffractometer with graphite-monochromated Cu-Kα radiation, and X-ray data for **5** were collected at Manchester using a Bruker SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation.

Cyclopenta(1,4-phenylenesulfone) (2)

4,4′-Bis(4-chlorobenzenesulfonyl)diphenylsulfide. A mixture of diphenyl sulfide (12.10 g, 0.065 mmol) and 4-chlorobenzenesulfonyl chloride (33.70 g, 0.180 mmol) in 1,2,4-trichlorobenzene (6 mL) was heated under nitrogen with stirring to 120 °C. Anhydrous iron(III) chloride (0.100 g) was added and the temperature was raised to 150 °C. When evolution of HCl had ceased, the solution was cooled and added to vigorously stirred acetone (150 mL) to give a solid which was recovered by filtration, washed with acetone, dried, and finally recrystallised from toluene (200 mL, containing 5 mL of acetylacetone to sequester residual iron) to give colourless 4,4′-bis(4-chlorobenzoyl)diphenylsulfide, m.p. 236 °C (27.8 g, 80% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, J = 8.4 Hz, 4H), 7.88 (d, J = 8.5 Hz, 4H), 7.53 (d, J = 8.4 Hz, 4H), 7.45 (d, J = 8.5 Hz, 4H); m/z (EI) 535 (100%, M^+). Anal. calcd. for $C_{24}H_{16}O_4Cl_2S_3$: C, 53.03; H, 2.99; Cl, 13.29; S, 17.97. Found: C, 53.10; H, 3.05; Cl, 13.30; S, 17.96%.

‡ It was anticipated that the larger macrocyclic sulfones reported in the present paper, with their greater degrees of conformational freedom, would have higher entropies of dissolution and therefore higher solublities than macrocycle **1**. In practice however, the rigidity of the diarylene-sulfone linkages still proved sufficient to limit drastically the solubility of macrocycles **2** and **3**.

Trisulfide-disulfone macrocycle 5. A solution of 4,4′-bis(4-chlorobenzoyl)diphenylsulfide (5.16 g, 15.0 mmol) and 1,4-benzenedithiol (2.13 g, 15.0 mmol) in *N,N*-dimethylacetamide (DMAc, 100 mL) was added from a syringe-pump over 24 h to a vigorously stirred suspension of potassium carbonate (1.17 g, 8.50 mmol) in a refluxing mixture of DMAc (170 mL) and toluene (30 mL), under nitrogen, with continuous removal of water *via* a Dean–Stark trap. The mixture was then cooled, filtered, acidified with dilute HCl to pH 3, and poured onto ice. The precipitate was filtered off and extracted with boiling water and methanol, affording a crude product of which 2.0 g was subjected to gradient elution chromatography with dichloromethane/ethyl acetate on silica gel. Macrocycle **5** was obtained as a colourless crystalline solid, m.p. 354 °C (0.56 g, 28% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.87 (d, J = 8.4 Hz, 4H), 7.79 (d, J = 8.4 Hz, 4H), 7.60 (d, J = 8.4 Hz, 4H), 7.57 (d, J = 8.4 Hz, 4H), 7.01 (s, 4H); m/z (EI) 604 (100%, M^+). Anal. calcd. for $C_{30}H_{20}O_4S_5$: C, 59.60; H, 3.31; S, 26.49. Found: C, 59.73; H, 3.40; S, 26.52%.

Cyclopenta(1,4-phenylenesulfone) 2. To a stirred suspension of macrocycle **5** (0.25 g, 0.41 mmol) in a mixture of chloroform (7 mL) and trifluoroacetic acid (12 mL) at 50 °C was added 30% (v/v) hydrogen peroxide (10 mL) dropwise over 15 min, and the temperature was then raised to 60 °C. A clear solution formed initially, but then a white precipitate developed and after 3 h the solid was filtered off, washed successively with water and with methanol, and dried to give the all-sulfone macrocycle **2** (0.27 g, 95%) This compound showed no melting point up to 500 °C. ^{1}H-NMR ($CDCl_3$/CF_3COOD, 2:1 v/v, 300 MHz) δ 7.30 (s, 20H); m/z (FAB) 700 (100%, M^+). Anal. calcd. for $C_{30}H_{20}O_{10}S_5$: C, 51.42; H, 2.85; S, 22.85. Found: C, 51.48; H, 2.90; S, 22.90%.

Cyclobis(1,4-phenylenesulfonyl-4,4′-biphenylenesulfone) (3)

Disulfide-disulfone macrocycle 6. A solution of 4,4′-bis(4-chlorobenzenesulfonyl)biphenyl (5.03 g, 10.0 mmol) and 4,4′-biphenyldithiol (2.18 g, 10.0 mmol) in *N,N*-dimethylacetamide (DMAc, 100 mL) was added from a syringe-pump over 8 h to a vigorously stirred suspension of potassium carbonate (2.75 g, 20.0 mmol) in a refluxing mixture of DMAc (200 mL) and toluene (40 mL). The mixture was refluxed for a further 12 h and was then cooled, filtered, concentrated to *ca.* half volume, and added slowly with stirring to water (300 mL) containing concentrated hydrochloric acid (10 mL). The precipitated solid was filtered off and extracted successively with boiling water and boiling methanol, affording a crude product of which 2.0 g was subjected to gradient elution chromatography with dichloromethane/ethyl acetate on silica gel. Macrocycle **6** was obtained as a colourless crystalline solid, m.p. 466 °C (0.35 g, 18% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.94 (d, J = 8.4 Hz, 4H), 7.75 (d, J = 8.4 Hz, 4H), 7.67 (d, J = 8.3 Hz, 4H), 7.53 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.34 (d, J = 8.3 Hz, 4H); m/z (FAB) 649 (100%, $[M+H]^+$). Anal. calcd. for $C_{30}H_{20}O_4S_5$: C, 66.64; H, 3.72; S, 19.76. Found: C, 66.11; H, 3.48; S, 20.00%.

Tetrasulfone macrocycle 3. Macrocycle **6** (0.12 g, 0.18 mmol) was oxidised as described for the synthesis of macrocycle **2**, giving an essentially quantitative yield of **3**. This compound showed no melting point up to 550 °C. ^{1}H-NMR ($CDCl_3$/CF_3COOD, 2:1 v/v, 300 MHz) δ 8.04 (s, 8H), 7.95 (d, J = 8.6 Hz, 8H), 7.73 (d,

J = 8.6 Hz, 8H); m/z (FAB) 713 (100%, $[M+H]^+$). Anal. calcd. for $C_{36}H_{24}O_8S_4$: C, 60.65; H, 3.39; S, 17.98. Found: C, 60.45; H, 3.42; S, 17.71%.

Fluorene-based disulfide-disulfone macrocycle (7)

2,7-Bis(4-chlorobenzenesulfonyl)-9,9-dimethylfluorene. This compound was obtained by reaction of 9,9-dimethylfluorene (12.61 g, 0.065 mol) with 4-chlorobenzenesulfonyl chloride (33.70 g, 0.180 mol) under the conditions described above for the synthesis of 4,4′-bis(4-chlorobenzoyl)diphenylsulfide. The title compound was obtained as a white crystalline solid (27.53 g, 78% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.08 (s, 2H), 7.95-7.88 (m, 8H); 7.54 (d, J = 8.6 Hz, 4H), 1.32 (s, 6H); m/z (EI) 543 (100%, M^+). Anal. calculated for $C_{27}H_{20}Cl_2O_4S_2$: C, 59.66; H, 3.71; Cl 13.04; S 11.79. Found: C, 59.70; H, 3.74; Cl, 13.03; S, 11.80%.

Disulfide-disulfone macrocycle 7. This compound was obtained by reaction of 2,7-bis(4-chlorobenzenesulfonyl)-9,9-dimethylfluorene (8.15 g, 15.0 mmol) with 4,4′-biphenyldithiol (3.27 g, 15.0 mmol) under the conditions described above for the synthesis of macrocycle **5**. Macrocycle **7** was obtained as a colourless crystalline solid (0.28 g, 14% yield) by column chromatography of 2.0 g of the crude product with trichloroethene/dichloromethane/ethyl acetate on silica gel. ^{1}H NMR ($CDCl_3$/CF_3COOD, 2:1 v/v, 300 MHz) δ (ppm) 8.05 (d, 2H), 7.90 (d, 2H), 7.78 (s, 2H), 7.66 (d, $4H_d$), 7.54 (d, 4H), 7.43 (d, 4H), 7.32 (d, 4H) and 1.36 (s, 6H). m/z (EI) 689 (100%, M^+). Anal. calculated for $C_{39}H_{28}O_4S_4$: C, 77.99; H, 4.10; S 18.61. Found C, 77.98; H, 4.08; S, 18.60%.

Crystal data

2. $C_{30}H_{20}O_{10}S_5.3.75C_4H_9NO$, M = 1027.47, monoclinic, $P2_1/m$ (no. 11), a = 11.0349(4), b = 20.6530(5), c = 11.1727(5) Å, α = 110.111(2)°, V = 2391.05(15) Å^3, Z = 2 (C_s symmetry), D_c = 1.427 g cm^{-3}, μ(Cu-Kα) = 2.824 mm^{-1}, T = 183 K, Bruker P4/RA diffractometer; 3663 independent measured reflections (R_{int} = 0.0245), F^2 refinement, R_1(obs) = 0.046, wR_2(all) = 0.130, 2905 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 209 parameters. CCDC 737298.

3. $C_{36}H_{24}O_8S_4.COCl_2.2CHCl_3$, M = 1050.44, monoclinic, $P2_1/n$ (no. 14), a = 9.8261(19), b = 10.809(2), c = 20.350(4) Å, α = 93.555(16)°, V = 2157.2(7) Å^3, Z = 2 [C_i symmetry], D_c = 1.617 g cm^{-3}, μ(Cu-Kα) = 7.052 mm^{-1}, T = 173 K, colourless prisms, Bruker P4/RA diffractometer; 3397 independent measured reflections (R_{int} = 0.0459), F^2 refinement, R_1(obs) = 0.054, wR_2(all) = 0.151, 2739 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 124°$], 218 parameters. CCDC 737299.

5. $C_{30}H_{20}O_4S_5.CH_3OH$, M = 636.80, monoclinic, $P2_1/c$, a = 18.8662(12), b = 12.4037(8), c = 11.9873(8) Å, α = 97.805(1)°, V = 2779.2(3) Å^3, Z = 4, D_c = 1.522 g cm^{-3}, μ(Mo-Kα) = 0.460 mm^{-1}, T = 100 K, Bruker SMART CCD diffractometer; 6643 independent measured reflections (R_{int} = 0.0471), F^2 refinement, R_1(obs) = 0.057, wR_2(all) = 0.189, 5005 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 58°$], 362 parameters. CCDC 737300.

6. $C_{36}H_{24}O_4S_4.CH_2Cl_2$, M = 733.72, monoclinic, $P2_1/n$ (no. 14), a = 14.5898(11), b = 23.7421(19), c = 20.4841(7) Å, α = 93.522(5)°, V = 7082.1(8) Å^3, Z = 8 [3 independent complexes, 2 with C_i symmetry], D_c = 1.376 g cm^{-3}, μ(Cu-Kα) = 4.170 mm^{-1}, T = 293 K, Siemens P4 diffractometer; 10688 independent measured reflections (R_{int} = 0.0352), F^2 refinement, R_1(obs) = 0.070, wR_2(all) = 0.218, 6098 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 124°$], 848 parameters. CCDC 737301.

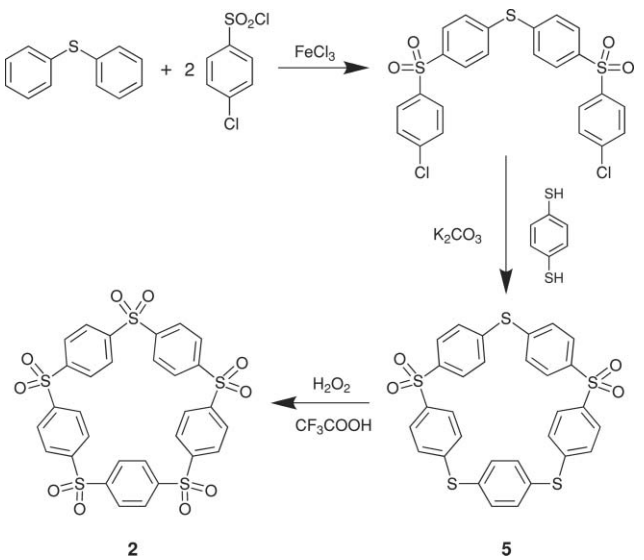
7. $C_{39}H_{28}O_4S_4.CH_2Cl_2$, M = 773.78, monoclinic, $P2_1/c$ (no. 14), a = 10.0673(10), b = 17.1131(16), c = 21.5403(16) Å, α = 96.428(7)°, V = 3687.7(6) Å^3, Z = 4, D_c = 1.394 g cm^{-3}, μ(Cu-Kα) = 4.034 mm^{-1}, T = 293 K, Siemens P4 diffractometer; 5229 independent measured reflections (R_{int} = 0.0461), F^2 refinement, R_1(obs) = 0.061, wR_2(all) = 0.169, 3419 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 120°$], 424 parameters. CCDC 737302.

Results and discussion

Synthesis of a pentagonal macrocyclic pentasulfone (2)

The C-S-C bond angle in an unstrained diarylsulfone is generally close to 105°.[17] This suggests that macrocycle **2**, if it could be obtained, should be a near-regular pentagon (internal bond angle 108°) with only a small degree of ring strain.

Moreover, as noted above, the diarylene sulfone units would tend to adopt "open book" conformations with the result that the molecule would be predicted to form a box-type structure. The macrocyclic pentasulfone **2** was obtained in a three-step synthesis (Scheme 1), *via* (i) bis-sulfonylation of diphenylsulfide with 4-chlorobenzenesulfonyl chloride, (ii) nucleophilic *cyclo*-condensation of the product with 1,4-benzenedithiol to give an intermediate trisulfide-disulfone macrocycle (**5**), and finally (iii) oxidation of **5** to pentasulfone **2** with hydrogen peroxide in trifluoroacetic acid.[18] Single crystal X-ray analyses (Fig. 2, 3 and 4) confirmed the proposed formulations of both macrocycles.



Scheme 1 Synthesis of macrocycles **2** and **5**.

In the crystal, one molecule of methanol is neatly encapsulated at the centre of macrocycle **5**, as shown in Fig. 2. The trisulfide-disulfone **5** has a rather irregular conformation in the solid state (Fig. 3), the tendency for diarylsulfone units to adopt open-book geometry (where C-C-S-C torsion angles = 90°) conflicting with the preferred symmetrically-skewed conformation (∠ C-C-C-S = ±30°) of the diarylsulfide linkage. In this molecule, the torsion angles at sulfone are 75/83 and 60/70°, and at sulfide they are 33/33, 42/65 and 14/72°. Bond angles (C-S-C) at sulfone are 103 and 104° and at sulfide are 102, 102, and 105°. There are no perceptible distortions of the S-Ar-S units in **5**, in contrast to the geometry of the strained tetrasulfone **1**, and its disulfide-disulfone precursor, in which the S-Ar-S groups are bowed outwards from collinearity by *ca.* 9°. Macrocycle **5** is thus, as predicted, essentially unstrained.

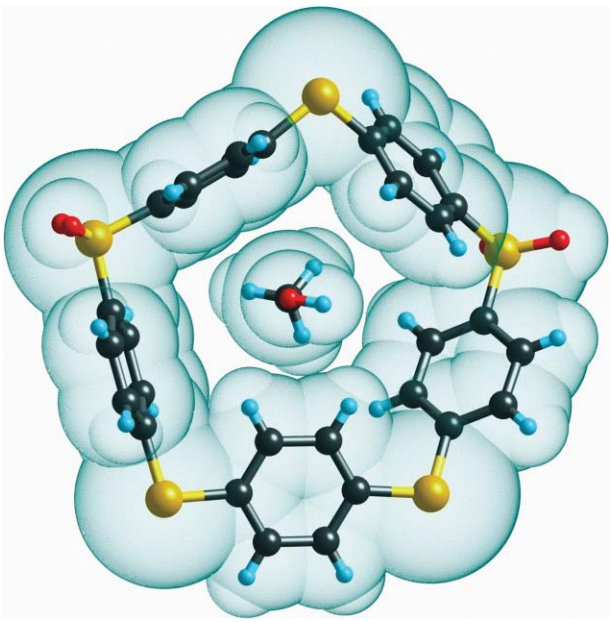


Fig. 2 Crystal structure of macrocycle **5** (methanol solvate) showing Van der Waals surfaces at 2.4 × CPK atomic radii.

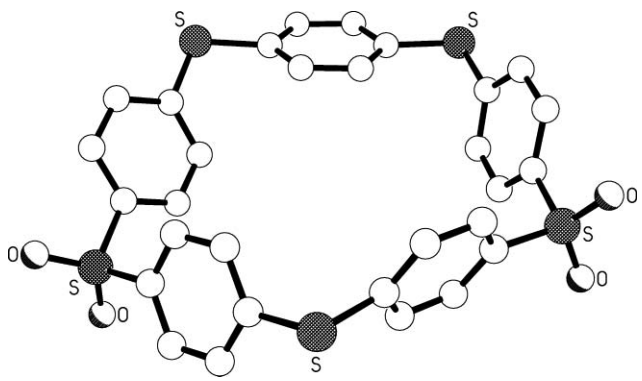


Fig. 3 Molecular structure of the trisulfide-disulfone macrocycle **5**.

The macrocyclic pentasulfone **2** adopts a very much more symmetrical structure than **5** in the crystal (Fig. 4), with all five diarylenesulfone moieties oriented approximately perpendicular to the mean (transannular) plane of the macrocycle. The five

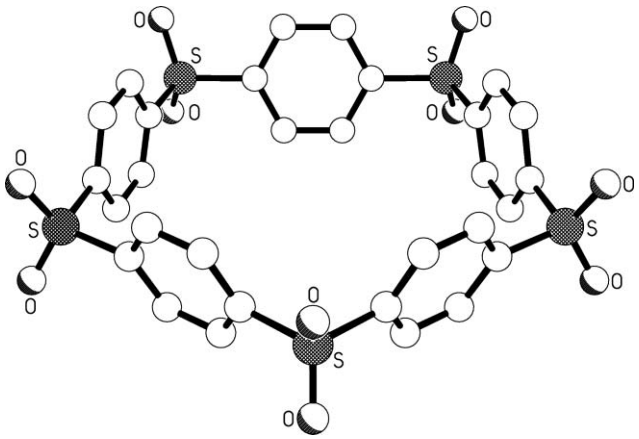
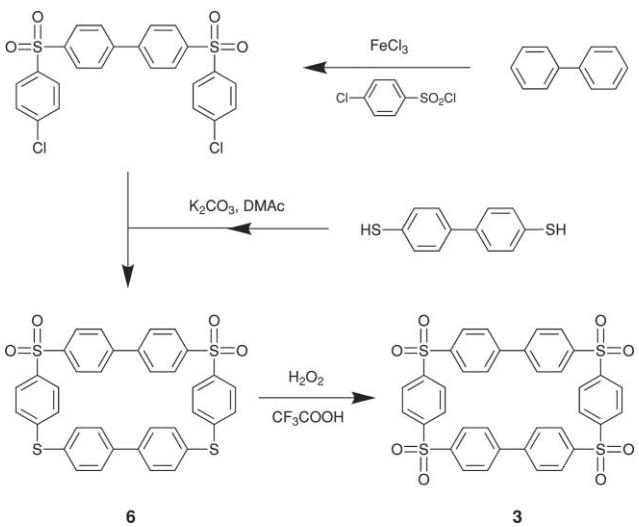


Fig. 4 Molecular structure of the macrocyclic pentasulfone **2**.

sulfur atoms are essentially coplanar, with no one sulfur lying more than 0.07 Å from their mean plane. Oxidation of the sulfide linkages to sulfone has clearly caused their attached aromatic rings to re-orient themselves into near-fivefold equivalence, though in the solid state the molecule has only twofold, mirror, symmetry. In Fig. 4, the crystallographic mirror plane would be vertical. Slight deviations from fivefold symmetry are represented by independent C-C-S-C torsion angles of 89, 85, 80, 78 and 69°, and C-S-C bond angles at 104.4, 104.6 and 105.9°. The true molecular symmetry of **2** is however demonstrated by its ^{1}H NMR spectrum ($CF_3CO_2D/CDCl_3$), which shows *just a single resonance* at 7.30 ppm, reflecting the equivalence of all 20 protons in the molecule.

Synthesis of a rectangular macrocyclic tetrasulfone (3)

The synthesis of the rectangular macrocyclic tetrasulfone **3** *via* its precursor disulfide-disulfone **6** is outlined in Scheme 2.



Scheme 2 Synthesis of the rectangular macrocycles **3** and **6**.

The oxidation step proceeded in essentially quantitative yield and afforded the rather insoluble macrocycle **3** in high purity. Single crystal X-ray structures for **6** and **3** are shown in Fig. 5 and 6 respectively. Solution of the structure of **6** was complicated by orientational disordering of the three crystallographically

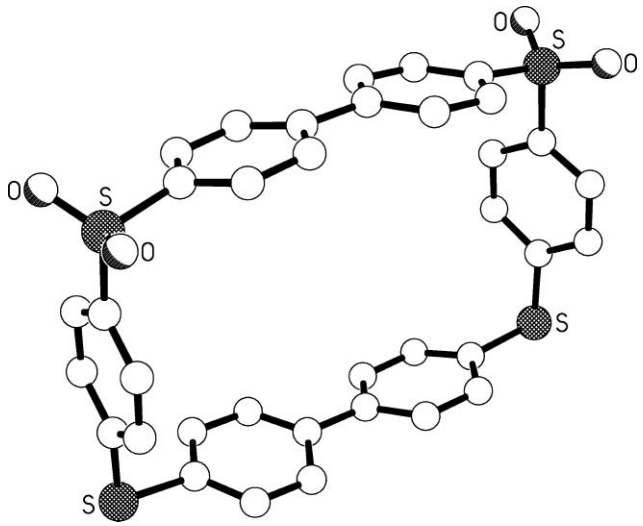


Fig. 5 Molecular structure of the macrocyclic disulfide-disulfone **6**.

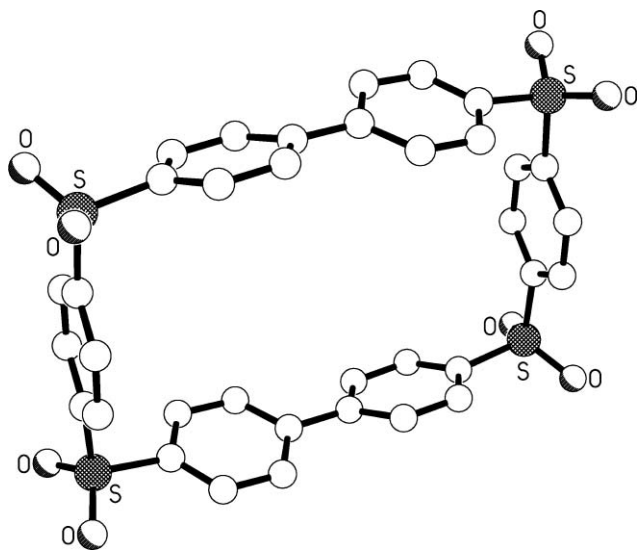


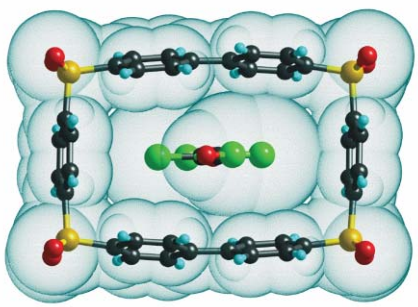
Fig. 6 Molecular structure of the macrocyclic tetrasulfone **3**.

independent molecules in the cell, resulting in apparent superposition of the sulfone and sulfide linkages. Ultimately this was resolved in terms of *ca.* 80/20 occupancy of the two orientations for one molecule and 50/50 occupancy for the other two molecules. Rotational disorder within the 4,4′-biphenylene units was also resolved. See ESI.†

The extensive disordering in the crystal structure of **6** reflects a marked similarity of conformation at the sulfone and sulfide units. The various C-C-S-C torsion angles thus lie in the narrow range 83-88°, indicating that here the "open book" conformation is adopted at both types of sulfur linkages, in contrast to the situation for macrocycle **5**. Bond angles (C-S-C) are markedly compressed (100.6-102.1°, c.f. 104.4-105.9°) in **5**, indicating significant ring-strain. This strain is also reflected in a substantial outward bowing of the biphenylene and phenylene units, the centroids of which lie 0.47 and 0.13 Å respectively outside the (almost perfect) rectangle defined by the four sulfur atoms.

The X-ray structure of tetrasulfone **3** shows a highly symmetrical macrocycle with an inversion centre at the centre of the cavity. The two independent C-S-C bond angles are 101.7 and 101.8°, again reflecting a significant degree of ring-strain. The degree of outward bowing of biphenylene and phenylene units is very similar to that observed in the precursor-molecule **6**, and the C-C-S-C torsion angles lie in the range 75-85°. Crystals of macrocycle **3** were grown by vapour diffusion of diethyl ether into a solution in chloroform-trifluoroacetic acid, and although the crystal lattice contains chloroform of solvation, the centre of the macrocycle is occupied by a molecule of *phosgene*, which is (necessarily) disordered about the inversion centre. This unexpected guest presumably arises from the well-known oxidation of chloroform in air, and is trapped in the macrocyclic cavity during crystallisation as a result of its complementary shape.

It is instructive to compare the geometry of the phosgene "complex" of macrocycle **3** with that of Stoddart's tetracationic 4,4′-bipyridinium-based macrocycle **4** in the form of its complex with tetrathiafulvalene.[19] Both supramolecules are shown in Fig. 7, drawn at the same scale. The close geometric analogy between the two systems, and the π-electron-deficient character of the macrocyclic tetrasulfone (arising from the presence of four strongly electron-withdrawing sulfone substituents) suggest that **3** could have significant potential as a complexing agent for electron-rich π-systems. However, in practice, its extreme intractability (m.p. >500 °C, soluble only in strong-acid solvent mixtures such as trifluoroacetic acid/chloroform) greatly limited the scope of complexation experiments, and a potentially more soluble, fluorene-based analogue (**8**) was therefore designed and its synthesis targeted (Scheme 3).



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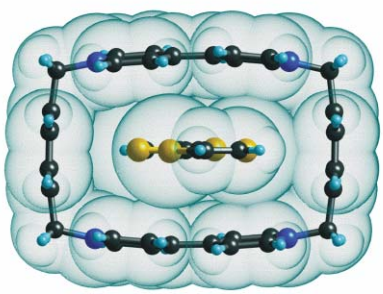

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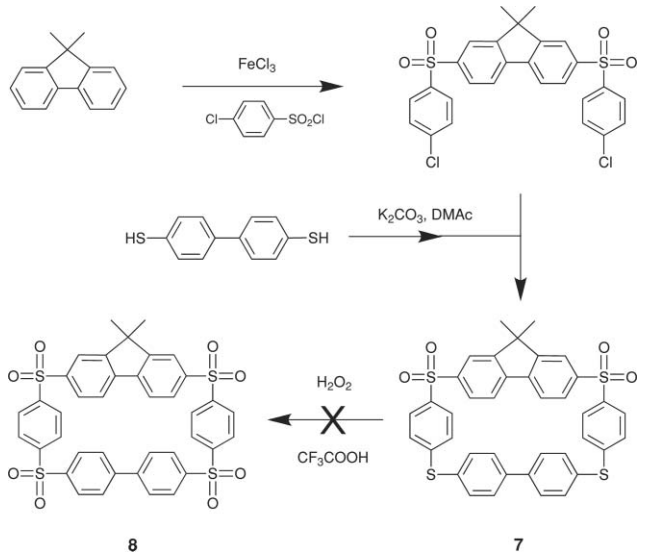
Fig. 7 Visual comparison of the structures of the tetrasulfone macrocycle **3** (encapsulating phosgene) and the bis-bipyridinium macrocycle **4** (as its tetrathiafulvalene complex). Van der Waals surfaces are shown at 2.4 × CPK atomic radii.



Scheme 3 Attempted synthesis of a the dimethyl-fluorene-derived macrocyclic tetrasulfone **8**. The final oxidation step led only to the formation of unidentified degradation products.

The initial sulfonylation and cyclisation steps proceeded in reasonable yield, with macrocycle **7** (the cyclic "monomer") being isolated from a mixture containing a series of higher macrocyclic oligomers. These were identified by MALDI-TOF MS up to the cyclic trimer, and the monomer, dimer and trimer were quantified by GPC as being formed in 24, 17, and 14% yields respectively. The molecular structure of **7** was confirmed by single crystal X-ray analysis (Fig. 8), which showed one of the two methyl groups oriented towards the centre of the macrocycle (and thus lying within the ring-current shielding zones of several aromatic rings) and the other directed outwards. The ^{1}H NMR spectrum of **7** however showed only a single methyl resonance, indicating rapid exchange of the two methyl environments (presumably by flipping about the C-S bonds) at ambient temperature. Attempted oxidation of **7** with hydrogen peroxide in trifluoroacetic acid, as carried out successfully with the all-aromatic disulfide-disulfone **6**, failed to yield the target tetrasulfone **8**. It is possible that acid-promoted ring-opening at the isopropylidene bridge under these conditions could lead to degradation of the aliphatic groups, and hence to more generalised decomposition of macrocycle **7**.

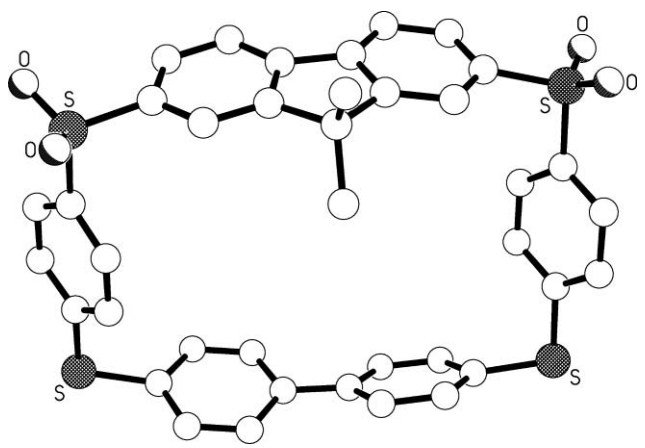


Fig. 8 X-Ray structure of the dimethylfluorene-based macrocycle **7**.

Conclusions

Two new, all-*para*, macrocyclic aromatic sulfones, **2** and **3**, have been successfully synthesised, with pentagonal and rectangular geometries respectively. Full characterisation data, including single-crystal X-ray structures, have been obtained for these compounds and their macrocyclic sulfide-sulfone precursors. Their box-like geometries and electron-deficient aromatic character suggest the possibility of their being able to act as receptors for electron-rich guest molecules. In practice however, their extreme insolubility limits the scope of binding studies to strong-acid solvents in which potential guests may be unstable. An attempt to enhance the solubility of macrocyclic sulfones by introducing the dimethylfluorenylene residue lead only to degradation during the oxidation stage (sulfide to sulfone) of the synthesis. It should be noted that the structural concepts developed in this work have also been applied to the design of unsymmetrical diimide-disulfone macrocycles. A number of these latter compounds show moderate (though still not good) solubility in organic solvents, and significant binding capabilities for molecules such as pyrene and perylene which have electron-rich, aromatic π-systems (*e.g.* Fig. 9).[20]

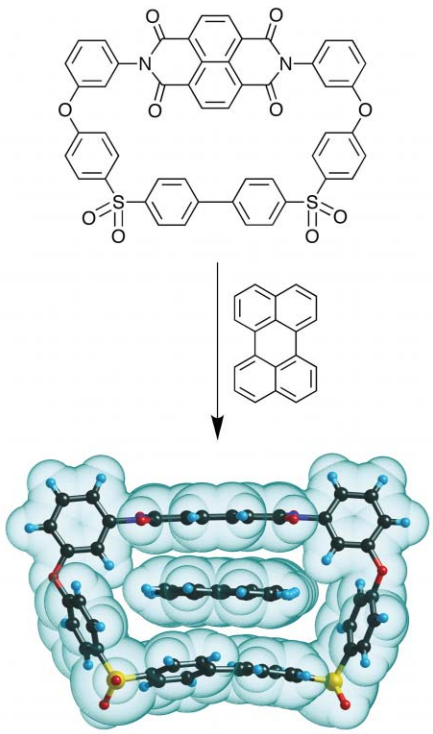


Fig. 9 Formation and X-ray structure of the complex between a macrocyclic diimide-disulfone and perylene.[8a] Van der Waals surfaces are shown at 2.4 × CPK atomic radii.

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